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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61K 7/48	A1	(11) International Publication Number: WO 97/20546 (43) International Publication Date: 12 June 1997 (12.06.97)
(21) International Application Number: PCT/US96/19405 (22) International Filing Date: 6 December 1996 (06.12.96) (30) Priority Data: 95870127.8 7 December 1995 (07.12.95) EP (34) Countries for which the regional or international application was filed: BE et al. (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): PETRI, Marco [IT/IT]; Via Ai Boschi, 70, I- 21021 Angera (IT). IAKOVIDES, Panos [GR/IT]; Piazza O. da Pordenone, 9, I-00145 Rome (IT). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).	(81) Designated States: CA, JP, MX, US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: USE OF HALOGEN BLEACH-COMPRISING COMPOSITIONS FOR IMPROVED MILDNESS TO THE SKIN (57) Abstract The present invention relates to the use of an organic or inorganic derived -NH ₂ compound, in a composition comprising a halogen bleach for improved skin mildness.		

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USE OF HALOGEN BLEACH-COMPRISING COMPOSITIONS FOR IMPROVED MILDNESS TO THE SKIN

Field of the Invention

The present invention is related to halogen bleach-based compositions.

Background of the Invention

Halogen bleaches, in particular hypochlorite, are known to be some of the most effective hygiene agents, especially at low concentrations, and are available in commercial quantities at acceptable cost. Halogen bleaches provide a hygiene benefit against a wide range of microbes including bacteria, moulds, yeast and fungi. Thus it is highly desirable to incorporate halogen bleaches in detergent compositions for bleaching and/or disinfection purposes. However, halogen bleaches and in particular hypochlorite are irritant and many consumers suffer from skin irritation when using such compositions.

Particularly, the hands of the user are prone to such irritation. As a result of coming into contact with such compositions the hands suffer from dryness and from a feeling of tightness. This occurs when the compositions are used neat and also when used in diluted form.

Without being limited by theory, it is believed that halogen bleaches like hypochlorite attack the uppermost layer of the epidermal of the skin. This results in the decrease of the elasticity of the skin. The skin also becomes more sensitive, resulting in dryness and coarseness of the skin. In addition, the skin may become inflamed and become red, sore and itchy. These effects are magnified in alkaline conditions, because alkali is also an irritant. Alkalinity is required for example for hypochlorite stability, thus alkaline pH is the preferred condition for hypochlorite-comprising compositions. However, alkaline conditions contribute to skin tightening because they alter the natural pH of the skin.

The object of the present invention is to improve skin mildness and reduce skin irritation of halogen bleach-comprising compositions.

The present invention overcomes these problems by the use of an organic or inorganic derived -NH_2 compound in a composition comprising a halogen bleach. Indeed, it has been found that a liquid composition comprising a halogen bleach and an organic or inorganic derived -NH_2 compound delivers improved skin mildness as compared to the same composition without said organic or inorganic derived -NH_2 compound, when used for instance by the user for hard-surfaces cleaning applications.

EP-A-644 256 discloses the use of the combination of an amine oxide with an alkyl sulphate in hypochlorite-comprising compositions for improved skin mildness. Said amine oxide is according to the formula $\text{R}_1\text{R}_2\text{R}_3\text{NO}$, wherein R_1 is a C_8 to C_{18} alkyl group and R_2 and R_3 are independently C_1 to C_3 alkyl groups. Said alkyl sulphate is according to the formula $\text{R}_4\text{OSO}_3\text{H}$, wherein R_4 is a C_6 to C_{10} alkyl group. No organic or inorganic derived -NH_2 compounds such as sulphamic acid are disclosed therein nor their skin mildness benefit.

Compositions comprising a halogen bleach and an organic or inorganic derived -NH_2 compound such as sulphamic acid are already known. However, none of the prior art documents discloses the benefit associated to the use of an organic or inorganic derived -NH_2 compound in a halogen bleach-comprising composition, i.e. improved mildness to skin and/or

reduced skin irritation, see for instance Japanese Kokai 63-108099, US 2,438,781, US 3,749,672.

Summary of the Invention

The present invention encompasses the use of an organic or inorganic derived -NH_2 compound in a composition comprising a halogen bleach, for improved skin mildness.

Detailed Description of the Invention

The present invention is the use of an organic or inorganic derived -NH_2 compound in a composition comprising a halogen bleach, for improved skin mildness.

Thus an essential ingredient in the present invention is a halogen bleaching agent or mixtures thereof. Common among these types of bleaches are the alkali metal and alkali earth metal hypochlorites, hypobromites and hypoiodites although other bleaches that are organic based sources of halide, such as chloroisocyanurate, are also applicable. Preferred bleach has the formula $\text{M}(\text{OX})_y$ where : M is a member selected from the group consisting of sodium, lithium, potassium, magnesium, calcium, and mixtures thereof; O is an oxygen atom; X is a member selected from the group consisting of chlorine, bromine, iodine, and mixtures thereof; and y is 1 or 2 depending on the charge of M. The preferred embodiment of the invention will effectively contain hypochlorite or hypochlorite and hypobromite.

The preferred hypohalite bleaches that comprise the present invention are sodium hypochlorite, potassium hypochlorite, calcium hypochlorite, magnesium hypochlorite, sodium hypobromite, potassium hypobromite, calcium hypobromite, magnesium hypobromite, sodium hypoiodite and potassium hypoiodite, more preferably sodium hypochlorite, potassium hypochlorite, calcium hypochlorite, magnesium hypochlorite, most

preferably sodium hypochlorite. A preferred organic-based bleach is chloroisocyanurate, however, any organic halide that produces active halogen is suitable for use in the present invention.

The compositions of the present invention comprise from 0.01% to 10% by weight of the total composition of said halogen bleach or mixtures thereof, preferably from 0.01% to 5%, more preferably from 0.1% to 2.5%, and most preferably from 0.5% to 2.5% by weight.

Another essential ingredient in the present invention is an organic or inorganic derived $-NH_2$ compound, or mixtures thereof. Said organic and inorganic derived $-NH_2$ compounds are effective in reducing or eliminating the irritation of the skin of the user, when a halogen bleach-comprising composition comprising it comes into contact with the skin. Examples of such compounds are sulphamic acid, sulphamide, p-toluenesulphonamide, imidodisulphonamide, benzenesulphonamide, melamine, cyanamide, alkyl sulfonamides, and mixtures thereof. At pH levels of the present invention, which are preferably greater than 11, the above mentioned compounds may be de-protonated, that is, they may be in the form of a salt and therefore due to expediency, ease of synthesis or preparation, or due to formulation practices the salt form of any or all of the above mentioned compounds will suffice. Although any suitable cation will suffice for the purposes of the present invention, sodium, potassium, lithium, magnesium, calcium, and mixtures thereof are preferred.

The present invention comprises said $-NH_2$ compounds in amounts such that the mole ratio of said halogen bleach to said $-NH_2$ compounds is from 10:1 to 1:10, preferably from 5:1 to 1:2, more preferably from 3:1 to 1:2.

The compositions according to the present invention are formulated in the alkaline pH range. Indeed, alkalinity plays an important role in the stability of said compositions. Accordingly, the compositions according to the present invention have a pH that is greater than 10, preferably greater than 11, more preferably greater than 12. This is achieved by the addition of a

caustic alkali or mixtures thereof such as sodium and/or potassium hydroxide.

The compositions according to the present invention are liquid compositions. Said liquid compositions are preferably but not necessarily formulated as aqueous compositions.

According to the present invention the compositions herein can optionally include a number of additional ingredients. Suitable optional ingredients include one or more other detergent adjunct materials or other materials for assisting or enhancing cleaning performance, treatment of the surface to be cleaned, or to modify the aesthetics of the composition (e.g. perfumes, colorants, dyes, etc.). The following are illustrative examples of such adjunct materials but are not meant to be exclusive or limiting in scope.

The compositions according to the present invention may contain from 0.1% to 95% by weight of a surfactant selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic surface active agents, preferably from 0.1% to 20% by weight.

Suitable anionic surfactants include anionic surfactants that can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfonation reaction products having in their molecular structure an alkyl radical containing from about 6 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of the anionic synthetic detergents which can form the surfactant component of the compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₆₋₁₈ carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, (the alkyl radical can be a straight or branched aliphatic chain); sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or

potassium salts of sulfuric acid ester of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut alcohols) and about 1 to about 10 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms; the reaction products of fatty acids are derived from coconut oil sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil and sodium or potassium beta-acetoxy- or beta-acetamido-alkanesulfonates where the alkane has from 8 to 22 carbon atoms.

Additionally, secondary alkyl sulfates may be used by the formulator exclusively or in conjunction with other surfactant materials and the following identifies and illustrates the differences between sulfated surfactants and otherwise conventional alkyl sulfate surfactants. Non-limiting examples of such ingredients are as follows.

Conventional primary alkyl sulfates, such as those illustrated above, have the general formula $\text{ROSO}_3\text{-M}^+$ wherein R is typically a linear $\text{C}_6\text{-C}_{22}$ hydrocarbon group and M is a water solubilizing cation. Branched chain primary alkyl sulfate surfactants (i.e., branched-chain "PAS") having 8-20 carbon atoms are also known; see, for example, Eur. Pat. Appl. 439 316, Smith et al., filed January 21, 1991.

Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbon "backbone" of the molecule. Such materials may be depicted by the structure



wherein m and n are integers of 2 or greater and the sum of m+n is typically about 9 to 17, and M is a water-solubilizing cation.

In addition, the selected secondary (2,3) alkyl sulfate surfactants used herein may comprise structures of formulas I and II



I



II

for the 2-sulfate and 3-sulfate, respectively. Mixtures of the 2- and 3-sulfate can be used herein. In formulas I and II, x and $(y+1)$ are, respectively, integers of at least about 6, and can range from about 7 to about 20, preferably from about 10 to about 16. M is a cation, such as an alkali metal, ammonium, alkanolammonium, triethanol-ammonium, and the like, can also be used.

The aforementioned secondary alkyl sulfates are those prepared by the addition of H_2SO_4 to olefins. A typical synthesis using alpha olefins and sulfuric acid is disclosed in U.S. Pat. No. 3,234,258, Morris, issued February 8, 1966 or in U.S. Pat. No. 5,075,041, Lutz, issued December 24, 1991. The synthesis conducted in solvents which afford the secondary (2,3) alkyl sulfates on cooling, yields products which, when purified to remove the unreacted materials, randomly sulfated materials, unsulfated by-products such as C10 and higher alcohols, secondary olefin sulfonates, and the like, are typically 90+ % pure mixtures of 2- and 3-sulfated materials (some sodium sulfate may be present) and are white, non tacky, apparently crystalline, solids. Some 2,3-disulfates may also be present, but generally comprise no more than 5% of the mixture of secondary (2,3) alkyl mono-sulfates. Such materials are available under the name "DAN", e.g. "DAN 200" from Shell Oil Company.

Other suitable surfactants to be used herein include amine oxides according to the formula $R_1R_2R_3NO$ where R_1 is primarily a C₆-C₂₂ alkyl group and R_2 and R_3 are C₁ to C₃ alkyl groups or mixtures thereof. Indeed, such amine oxides for use herein can be Genaminox^R LA, Gemaminox^R MY-X (available from Hoechst), C₁₂-C₁₄ Aromox^R DMMCO-W, (AKZO), Aromox DM14D-W, (AKZO) and Aromox DM14D-W (AKZO). Suitable amine oxides for use herein are preferably halogen bleach compatible.

Other optional ingredients such as buffers can be included in the formulations herein for a variety of purposes. One such purpose is to adjust the cleaning solution pH to optimize the hard surface cleaner composition's effectiveness relative to a particular type of soil or stain.

Buffers may be included to stabilize the adjunct ingredients with respect to extended shelf life or for the purpose of maintaining compatibility between various aesthetic ingredients. The hard surface cleaner of the present invention optionally contains buffers to adjust the pH in a preferred range above 11. Non-limiting examples of such suitable buffers are potassium carbonate, sodium carbonate, and trisodium phosphate, however, the formulator is not restricted to these examples or combinations thereof.

The compositions according to the present invention may also optionally contain one or more iron and/or manganese chelating agents. Examples of such compatible chelating agents are ethane-1-hydroxy-1, 1-diphosphonic acid (EDHP) and dipicolinic acid.

Perfumes are an optional but highly preferred ingredient especially for the liquid composition embodiment. Perfume is usually used at levels of from 0% to 5%. In U.S. Pat.No. 4,246,129, Karcher, issued January 20, 1981 (incorporated herein by reference), certain perfume materials are disclosed which perform the added function reducing the solubility of anionic sulfonate and sulfate surfactants.

As a further optional, but preferred ingredient, the present compositions comprise bleach boosters. Bleach boosters are those compounds that in an alkaline pH environment are capable of releasing a halide ion, undergoing an oxidation, a reduction or other disproportionation that otherwise yields an activated halide ion. Typically boosters containing bromine atoms and iodine atoms are used in the presence of chlorine atom based bleaches and iodine is used when bromine based bleaches are employed as the primary bleaching agent. Preferred bleach booster has the formula $M(X)_y$ where : a) M is a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, copper, zinc, and mixtures thereof; and b) X is the radical bromide, hypobromite, bromate, iodide, hypiodite, iodate, and mixtures thereof; wherein y is 1 or 2.

While not wishing to be limited by theory, it is believed that the boosters have the effect, as in the case of hypochlorite based bleach, of converting the hypochlorite bleach into a more reactive and/or a more stable species, for example, hypobromite, thus providing for the full utility of the bleach formulated. Bleach boosters of the present invention may be added as a precursor which itself can be a bleach booster, for example, iodide ion is a suitable bleach booster according to the present invention. The boosters thus formed by oxidation/reduction or other disproportionations, for example, iodate, may be instead added directly.

The bleach boosters of the present invention are of the formula MX where M is a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, copper, and zinc while the X is halogen. The preferred bleach boosters are the sodium and potassium salts of bromine and iodine, more preferably sodium and potassium bromide and iodide.

The present invention comprises bleach boosters that are present such that the mole ratio of bleach to bleach booster is from 1:0.1 to 1:2, preferably from 1:0.2 to 1:1.

Other optional ingredients employed in the compositions according to the present invention can be selected from bleach stabilizers, pigments, color speckles, other suds boosters, suds suppressors, anti-tarnish and/or anti-corrosion agents, soil-suspending agents, germicides, alkalinity sources, hydrotropes, anti-oxidants, clay soil removal/anti-redeposition agents, polymeric dispersing agents, or mixtures thereof.

The present invention will be further illustrated by the following examples.

EXAMPLES

The following compositions are made by mixing the following ingredients in the listed proportions (weight %). All these compositions were found to be particularly mild to the skin when used both under neat and diluted conditions.

COMPOSITIONS

Ingredients (weight%)	I	II	III	IV	V	VI	VII	VIII
Sodium Lauryl sulfate	2	1	-	4	4	0.5	-	-
Sodium Octyl sulfate	-	-	-	2	2	-	1	1.5
Lauryl dimethyl amineoxide	-	-	0.8	-	-	0.6	2	1
LAS	-	0.5	-	-	-	-	-	-
Silicate	-	-	0.2	0.1	0.1	-	0.5	0.5
Perfume	-	0.1	-	0.3	0.3	-	0.3	0.3
Caustic	2	3.2	2	3	3	2.2	2.8	2.5
Sulfamic acid	2.5	3.5	1.5	2.9	2.9	4.0	2.2	2.0
Sodium bromide	-	0.5	0.3	-	0.5	0.8	0.5	0.5
Hypochlorite	1.5	2.0	1.0	1.7	1.7	3.0	1.5	1.3
Water and minors up to 100%								


WHAT IS CLAIMED IS:

1. The use of an organic or inorganic derived -NH_2 compound, in a composition comprising a halogen bleach, for improved skin mildness.
2. The use according to claim 1 wherein said composition has a pH greater than 10, preferably greater than 11 and more preferably greater than 12.
3. The use according to any of the preceding claims wherein said halogen bleach has the formula $\text{M}(\text{OX})_y$ where :
 - a) M is a member selected from the group consisting of sodium, lithium, potassium, magnesium, calcium, and mixtures thereof;
 - b) O is an oxygen atom; and
 - c) X is a member selected from the group consisting of chlorine, bromine, iodine, and mixtures thereof;wherein y is 1 or 2.
4. The use according to any of the preceding claims wherein said composition comprises from 0.01% to 10% by weight of said halogen bleach or mixture thereof, preferably from 0.01% to 5% and more preferably from 0.1% to 2.5%.
5. The use according to any of the preceding claims wherein said -NH_2 compound is a member selected from the group consisting of sulphamic acid, sodium sulphamate, potassium sulphamate, sulfamide, p-toluenesulphonamide, imidodisulphonamide, benzenesulphonamide, melamine, cyanamide, alkyl sulfonamide, and mixtures thereof and preferably is sulphamic acid.
6. A composition according to the preceding claims wherein the molar ratio of bleach to said -NH_2 compound is from 10:1 to 1:10, preferably from 5:1 to 1:2, and more preferably from 3:1 to 1:2.
7. The use according to any of the preceding claims wherein said composition further comprises from 0.1% to 95% by weight of a deterative surfactant.

8. The use according to any of the preceding claims wherein said composition further comprises optional ingredients selected from the group of buffers, chelating agents, perfumes, bleach stabilizers, pigments, color speckles, suds boosters, suds suppressors, anti-tarnish and/or anti-corrosion agents, soil-suspending agents, germicides, alkalinity sources, hydrotropes, anti-oxidants, clay soil removal/anti-redeposition agents, polymeric dispersing agents, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/19405

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) :A61K 7/48 US CL :424/62 According to International Patent Classification (IPC) or to both national classification and IPC																				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 424/62 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)																				
C. DOCUMENTS CONSIDERED TO BE RELEVANT																				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																		
X	US 4,822,512 A (AUCHINCLOSS) 18 April 1989, columns 1-2.	1-3																		
Y	US 3,060,097 A (FELLOWS) 23 October 1962, columns 1-2.	1-3																		
Y	US 2,283,350 A (BAUM) 19 May 1939, columns 1-2.	1-3																		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.																				
<table border="0"><tr><td>* Special categories of cited documents:</td><td>*T</td><td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention</td></tr><tr><td>*A* document defining the general state of the art which is not considered to be of particular relevance</td><td>*X*</td><td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td></tr><tr><td>*B* earlier document published on or after the international filing date</td><td>*Y*</td><td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td></tr><tr><td>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)</td><td>*A*</td><td>document member of the same patent family</td></tr><tr><td>*O* document referring to an oral disclosure, use, exhibition or other means</td><td></td><td></td></tr><tr><td>*P* document published prior to the international filing date but later than the priority date claimed</td><td></td><td></td></tr></table>			* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention	*A* document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	*B* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)	*A*	document member of the same patent family	*O* document referring to an oral disclosure, use, exhibition or other means			*P* document published prior to the international filing date but later than the priority date claimed		
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Date of the actual completion of the international search 24 MARCH 1997		Date of mailing of the international search report 04 APR 1997																		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer SALLY GARDNER  Telephone No. (703) 308-2351																		

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/19405

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-8
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1))(July 1992)*